P.E.I.'s MOST PRECIOUS RESOURCE

PESTICIDE SAMPLING PROJECT

(to March 31, 1991)

Groundwater Program, Canada/P.E.I.

Management Agreement

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THE CANADA – PRINCE EDWARD ISLAND
WATER MANAGEMENT AGREEMENT

Environment Canada Environnement Canada

Prince Edward Island
Department of the Environment

EXECUTIVE SUMMARY

During the course of this, the second phase of the pessicide sampling project, four pesticides atrazine, chlorothalonil and mancozeb were investigated. Although not part of the original survey design metribuzin was analyzed on several occasions. Seventy four samples from forty three sites were analyzed. Sample collection conducted by the PEI Department of the Environment included samples for pesticides, total coliform, and nitrate. Well construction information was collected wherever possible. Pesticide analysis was carried out by the Atlantic Veterinary College (AVC) Toxicology Laboratory. Bacteria and nitrate analysis were conducted by the Environmental Services Lab and the PEI Department of Agriculture Soil and Feed Lab, respectively. Spiked samples were provided by Environment Canada, Moncton, New Brunswick and Rohm and Haas Canada Inc., West Hill, Ontario.

Residues from each pesticide were detected, with 13 samples reporting the presence of pesticide residue. Fifteen samples were analyzed for atrazine, of these five contained a detectable residue. Two samples with trace concentrations of chlorothalonil were detected from the 25 samples analyzed. Mancozeb was detected in 4 of 21 samples analyzed and metribuzin in 2 of 3 samples. All detections were well below the recommended guidelines and guidance values from the Canadian Drinking Water Quality Guidelines(1989) and Health and Welfare Canada. There is no guideline or guidance value for mancozeb.

The rapid decompostion of mancozeb contributed to problems with the analytic procedure. As a result, the reported values for mancozeb are uncertain. These values are expressed as the EBDC mancozeb equivalent.

Results from nitrate samples indicated that the average nitrate concentration in samples with detectable pesticide concentrations is higher than the average of all 43 sites. The results are comparable to the results obtained in a companion study of nitrate concentrations in areas of different landuse.

Due to the lack of information on well construction it was not possible to correlate results from nitrate, total coliform, pesticide residue, and well construction.

The frequency of detection in the samples indicates the need for continuing monitoring of pesticides in PEI groundwater. Metabolites of pesticides with rapid degradation should be considered in the analysis along with the parent compound. Additional development of improvement in laboratory protocol, including lab reference standards, is warranted. Drinking water guidelines should be developed for chemicals without guidance values.

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PESTICIDES SAMPLING PROJECT

1.0 INTRODUCTION

Agriculture is extremely important to the economy of Prince Edward Island, accounting for 9.5 per cent of the Provincial Gross Domestic Product in 1989. The total value of farm cash receipts amounted to $253.9 Million with the sale of potatoes accounting for 46.9% of the total farm cash receipts (P.E.I. Dept. of Finance, March, 1990).

The use of pesticides in the province is dominated by the potato industry. From 1981-1989, the average potato acreage grown was 68,100 acres which represents approximately 5 per cent of the total land of the province. In certain districts of the province i.e. East Prince County, the percentage of land area in potatoes would be nearer 10%. Typically a potato crop receives an application of pesticides seven (7) times during the growing season. These applications are required to control insects, weed, fungus and other pests.

While it is recognized that the use of chemical pesticides is necessary under current agricultural practices, there is concern that some of these pesticides are entering Island groundwater.

The province is characterized by shallow, often permeable overburden, overlying a fractured sandstone aquifer. Fracture aperture and frequency in the bedrock decrease with depth (Francis, 1981), thus the most productive water bearing zones are in the shallow bedrock, which are also the most vulnerable zone to contamination. Previous sampling in the province has determined that approximately 30 wells had detectable (>1.0 ppb) residues of aldicarb (Matheson et al, 1987). This occurrence is entirely related to the growing of potatoes.

The Pesticide Sampling Project is one of three groundwater projects conducted under the Canada/Prince Edward Island Water Management Agreement initiated in 1987. The intent of the project was to investigate the impact of normal pesticide application on groundwaters in areas of agricultural landuse. To this end, wells were selected on a "worst case" basis adjacent to areas of pesticide use.

Phase I of the Pesticide Sampling Project commented on the occurrence of dinoseb in groundwater supplies in the communities of Tignish and Kensington. In each case these occurrences were traced to spills of the pesticide. While the Tignish and Kensington dinoseb investigations continued during the survey, this data is not included in this report, as these occurrences do not reflect the normal application of pesticides on agricultural lands.

A technical advisory committee provided general guidance for the project, which proceeded in two phases. The first phase of sampling extended from October of 1988 to August 1989, and included the collection of approximately 145 samples. The second phase of sampling was conducted from November of 1990 to March 1991, with the collection of 74 samples from 43 sites. In addition to pesticides, samples were collected for nitrate, and total coliform.

2.0 PESTICIDE SELECTION

Toxicity, water solubility and amount in use were the main criteria for pesticide selection. The fungicides chlorothalonil and mancozeb and herbicide atrazine were chosen principally because of their widespread use and high water solubility. Atrazine, which is used mainly for cereal crops, has been detected in groundwater investigations in other jurisdictions. Metribuzin was not included in the original survey design, however where compatible with the analysis of other parameters such as chlorothalinol, analysis for metribuzin was performed. Table 1 presents some of the characteristics of these pesticides.

Table 1: Characteristics of Pesticides Chosen for Pesticide Sampling Program

Pesticide	Water Solubility	LD Oral (mg/Kg)*	Persistence (weeks)	Approximate Quantity Used (Kg)**
Atrazine	70 mg/L (22°C)	3080	28 - 52	7700
Chlorothalonil	1.2 mg/L (25°C)		> 10000	
Mancozeb				
Metribuzin	1200 mg/L (25°C)	1937-2345	3 - 16	18600

*Values refer to laboratory tests with rats.

**It was very difficult to obtain the quantity used for these pesticides as chemical companies and government agencies tend to treat this information as confidential. The figures given in Table 1 are estimates based only on the most recently available information.

3.0 SITE SELECTION

The philosophy used in the selection of sites was a "worst case" scenario rather than a random sampling. Accordingly, wells judged to be most susceptible to pesticide contamination were chosen for sampling. Sites were selected in areas where the pesticides of interest were used. This information was obtained from the PEI Department to Agriculture, Agriculture Canada, pesticide retailers and the farmers using the chemicals. Farmers contacted for information regarding application rate, previous use patterns, etc. for a particular pesticide were generally co-operative.

In selecting these sites the following criteria were used:

1) the pesticide must have been applied within the past three years;

2) The well must be downslope or relatively close (within 300 meters) to a field upon which the pesticides have been applied;

In selecting the sites no attempt was made to choose wells of particular construction. As a result wells of varying construction are represented with a range of well depths and casing lengths.

In all a total of 43 wells were selected throughout the province with the greatest concentration of these being in the major potato producing areas of the province. The geographical distribution of the sites is displayed in Figure 1.

4.0 SAMPLING PROGRAM

Sampling was conducted by staff of the Prince Edward Island Department of the Environment. The water samples were collected, when possible, from an inside tap nearest to the pumping device, but occasionally samples were obtained from an outside tap. The water was run for a minimum of 5 minutes before collecting the sample to ensure it was obtained from the well. All samples were collected from actively used private wells.

The one litre amber glass pesticide sampling bottles were prepared with an acetone and hexane rinse. An aluminum foil cap liner was also prepared this way and used on each bottle. Samples were kept cool until delivery to the laboratory within 24 hours of collection.

To provide some insight into the vulnerability of individual wells to contamination, samples for bacteria and nitrate were also collected at each site. The presence of bacteria in water supplies is an indication that near surface water may be gaining access to the well. A variety of sources, including a companion study conducted under the Canada P.E.I. Water Management Agreement, indicate elevated nitrate concentrations can frequently be correlated with agricultural activities.

Where available, information concerning well construction was recorded. Regrettably, information was available for only 9 of 43 wells sampled, and even here well information was rather sparse. Generally, it was not possible to obtain information regarding water levels in wells.

5.0 ANALYSES

The analyses of pesticide residues were performed by the Atlantic Veterinary College (AVC) Toxicology Laboratory in Charlottetown using a gas chromatography mass selective detector. The laboratory of the Water Quality Branch, Inland Waters, Environment Canada provided support by supplying spikes for the quality assurance/quality control program, and with the provision of general advice. Bacterial and nitrate analyses were conducted by the Environmental Services Lab of the P.E.I. Department of the Environment and the Agricultural Research Station Soil and Feed Lab respectively.

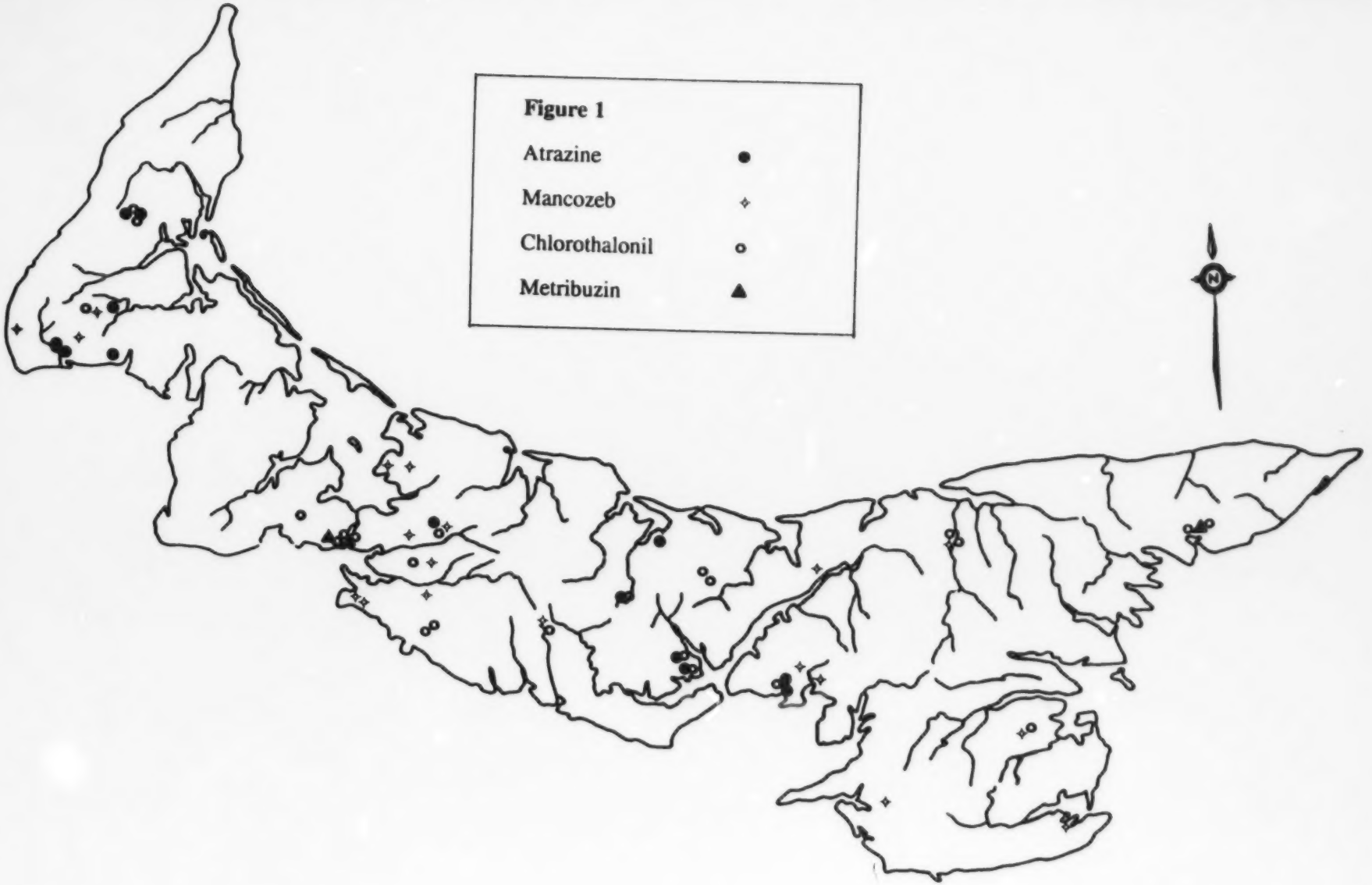


Figure 1
Atrazine
Mancozeb
Chlorothalonil
Metribuzin
N

6.0 QUALITY ASSURANCE/QUALITY CONTROL

The Quality Assurance/Quality Control (Q_A/Q_C) portion of the project was not as rigorous as in the previous phase. This is due to the use of only one laboratory for the analysis, the accuracy of previous results from this laboratory and the added cost of analysis for extra Q_A/Q_C samples.

The Q_A/Q_C component of the sampling and analytical work consisted of duplicate samples, blank samples and spiked samples. Two duplicate samples for each pesticide were analyzed by the A.V.C. Two spiked samples of both chlorothalonil and atrazine were prepared by the Environment Canada, Water Quality Branch in Moncton, New Brunswick. Rohm and Haas Canada Inc. of West Hill, Ontario prepared two spiked samples for mancozeb. Separate aliquots, of differing concentrations, were prepared at A.V.C. by diluting one of these spikes. Concentrations of the resulting spike samples are indicated in Table 3. Four blank samples of deionized water from the Environmental Services Lab were also analyzed. The results of the Q_A/Q_C program are presented in Tables 2 to 4.

Table 2 - Q_A/Q_C Duplicate Samples, A.V.C.

Sample #	Atrazine	Mancozeb	Chlorothalonil	Metribuzin
1685	N.D.		N.D.	
1686	N.D.		N.D.	
1721	N.D.	N.D.	N.D.	N.D.
1722	N.D.	N.D.	N.D.	N.D.
1727		N.D.		
1734	N.D.			

N.D. = Not Detected

The duplicates in Table 2 indicate all results were reported as not detectable by the AVC laboratory indicating that the laboratory was consistent in the duplicate samples. Since all the duplicate samples were non detectable, this is considered a less effective test of the precision of the lab, although the results are a fair reflection of the concentration of these pesticides in groundwater.

Table 3 - Q_A/Q_C, Spiked Samples, A.V.C.

Sample #	Atrazine (ppb)		Mancozeb (ppb)			Chlorothalonil(ppb)	
	Reported	Actual	Reported	Actual		Reported	Actual
1681	N.D.					5.50	5.24
1687	5.50	5.25				N.D.	
1700			32.0	200			
1702-A			20.10	100	Trace		
1702-F			N.D.	20			
1706			N.D.			24.20	21.05
1716	0.90	1.05	N.D.			N.D.	

N.D. = Not Detected

As shown in Table 3, samples spiked with atrazine and chlorothalonil indicated recoveries within an acceptable range. For atrazine and chlorothalonil, the maximum percent deviation from the actual concentration was 14.2% and 13.0% respectively. Trace levels of chlorothalonil were reported in sample 1702-A even though the sample was spiked with mancozeb only.

Mancozeb is a part of the ethylene-bis-dithiocarbamates (EBDC) chemical group. The AVC's method of analyses determines the total present in a sample, thus it is uncertain that the chemical results are actually mancozeb, only that the results portray chemicals within the EBDC chemical group. Mancozeb results are reported as EBDC mancozeb equivalents with a detection limit of 25 ppb, which is greater than the concentration in spike 1702-F.

The reported concentrations for the mancozeb spikes were well below the actual concentration of mancozeb in the spikes when they were prepared. Experimentation at the laboratory with mancozeb spikes indicated very rapid decompostion. Within five days of sample preparation the mancozeb recovery decreased by approximately 50 per cent. This decay seems to plateau with 10 to 20 per cent of the original concentration remaining in the sample.

The amount of time between the preparation and analysis of the spikes was approximately 12 weeks, and the reported concentrations of mancozeb were very low. Sample recovery ranged from approximately 20 per cent to 0% (below the detection limit).

Metribuzin was not intended as a part of the survey and was analyzed on a few occasions where analytic protocol for other pesticides allowed for the determination of metribuzin as well. Therefore, no spiked samples for metribuzin were prepared.

All blank samples were reported as non-detectable as presented in Table 4.

Table 4 - Q_A/Q_C, Blanks, A.V.C.

Sample #	Atrazine	Mancozeb	Chlorthalonil	Metribuzin
1676		N.D.		
1701		N.D.		
1702		N.D.		
1711		N.D.	N.D.	N.D.
1720	N.D.	N.D.	N.D.	N.D.

N.D. = Not Detected

7.0 RESULTS

a. Pesticides

The results of the 1990-91 survey is summarized in Table 5. Although there were some detectable residues for each of the pesticides sampled, all values are below guidelines and guidance values provided by Health and Welfare Canada, where such values have been determined. Currently there is no guideline or guidance value for mancozeb.

Atrazine was detected in 5 of the 15 samples analyzed, with a maximum concentration of 1.2 ppb.

Mancozeb was detected in 4 of the 21 samples analyzed. Three of the twenty- one analyses for mancozeb indicated detectable concentrations present, with concentrations ranging as high as 32 ppb. A fourth analysis indicated trace concentrations, but these results could not be confirmed. As noted earlier there were significant uncertainties relating to the accuracy of these analyses for mancozeb. Upon resampling of two of the sites with detectable levels of mancozeb 5 weeks later, no mancozeb was detected.

Table 5. Summary of Results of the 1990-91 Sampling Survey

Pesticide	# of Samples Analyzed	# of Detectable Results	Max.Conc. Reported (ppb)	Drinking Water Guidelines (ppb)	# of Results Over Guidelines
Atrazine	15	5	1.2	60[1]	0
Mancozeb	21	4	*see text	___[3] N/A	
Chlorothalonil	25	2	trace	30[2]	0
Metribuzin	3	2	6	80[1]	0

[1]Guidelines for Canadian Drinking Water Quality - 1989.

[2]Guidance Value as suggested by Health and Welfare Canada, in response to a specific problem and it has not received the thorough evaluation that would be given to a regular drinking water guideline".

[3]no value available.

Chlorothalonil was found at trace concentrations (below a level at which the concentration could be quantified) in 2 of the 25 samples analyzed.

While only three samples were analyzed for metribuzin, two of these samples indicated detectable concentrations of the compound. The maximum concentration reported for metribuzin was 6 ppb.

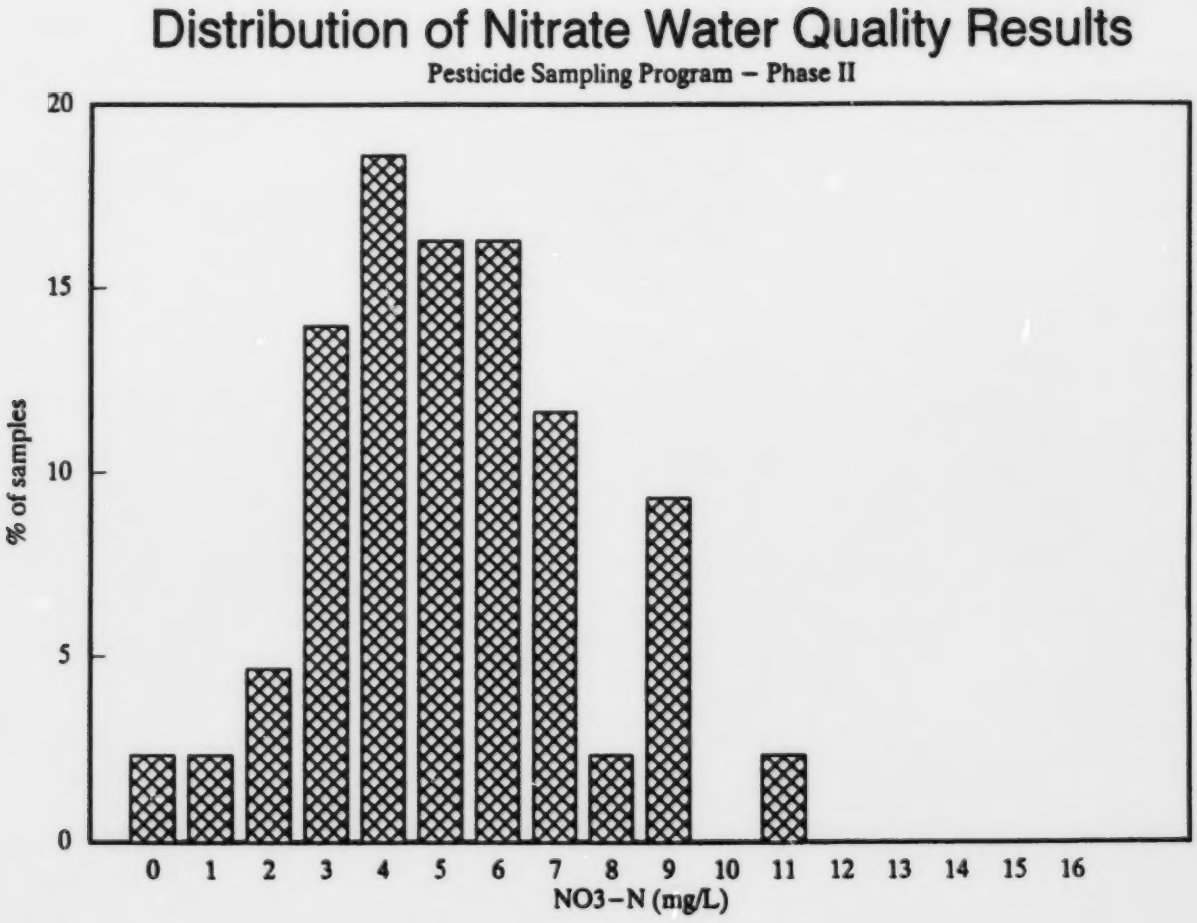
The detection limit for atrazine, chlorothalonil and metribuzin was 0.1 ppb. Detection limits for EBDC mancozeb equivalent was 25 ppb.

b. <u>Nitrate and Total Coliform</u>

Nitrate and bacterial water quality samples were collected at each sampling site to provide some insight into the relative vulnerability of the wells to contamination by surface and near surface waters, the assumption being that wells which are more vulnerable to these sources of contamination may also be more susceptible to other agricultural chemicals such as pesticides.

Figure 2 shows the distribution of nitrate concentrations for this survey. The average nitrate concentration for all 43 wells sampled was 4.8 mg/L NO_3-N, with values ranging from <0.2 mg/L to 11 mg/L. The average nitrate concentration of samples from the 13 wells with detectable pesticide concentrations was 5.9 mg/L, 1.1 mg/L higher than the average nitrate value for all samples

Figure 2


Distribution of Nitrate Water Quality Results
Pesticide Sampling Program – Phase II
% of samples
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
NO3–N (mg/L)

collected. These results are comparable to those from a companion study on nitrates also conducted under the Canada P.E.I. Water Management Agreement, in which nitrate concentrations in areas of different landuse were measured. In that study an average concentration of 5.57 mg/L was reported for wells constructed in areas of intensive row cropping. This is significantly higher than the provincial average of 2.5 mg/L.

Of the 42 sites sampled for coliform bacteria, only 5 had evidence of bacterial contamination. Three of these were cases of low counts, well below the 10 mpn/100 ml limit set out in the Guidelines for Canadian Drinking Water Quality. The remaining two samples had counts of 18 and 26 organisms per 100 mls. Samples from two of the five wells in which bacteria were found indicated the presence of some quantity of pesticide residue.

c. Influence of Well Construction

Well construction information was collected where possible, with the aim of identifying any relationship between well construction and susceptibility to contamination by agricultural chemicals. Unfortunately there is insufficient data to draw any meaningful conclusions in this regard, as information was available for only 9 out of 43 sites. Table 6 shows the information on well construction collected during the survey in the field.

Table 6: Well Information

Sample Number	Depth (m)	Casing Length (m)	S.W.L. (m)	Year Drilled	No_3-N (mg/l)	Pesticide Residue
1670	Shallow				3.6	N
1673	Shallow				11.0	Y
1675	Shallow				9.0	N
1688	21.3	6.1		1964	3.8	Y
1691	25.9			1975	5.2	Y
1695	24.4	13.4	12.2	1987	4.8	N
1697				Old	2.9	N
1722	7.6			Old	5.0	N
1730	21.3		9.1		3.8	N

8.0 DISCUSSION

Atrazine, chlorothalonil, mancozeb and metribuzin, were investigated during this project. Residues from each pesticide were detected with 13 sites reporting the presence of pesticide residues. All results were below the guideline or guidance value where such values are available, even though samples were collected on a worst case basis.

Trace levels of pesticides were detected in six samples. "Trace" concentrations refers here to a response below the quantifiable detection limit.

A third of the samples analyzed for atrazine contained detectable residues; however, the concentrations were well below the Canadian Drinking Water Guidelines of 60 ppb. Two of the five samples with detectable residues contained only trace levels.

Chlorothalonil was detected in only two of twenty five samples and these locations were at trace levels. There is no guideline value in the Canadian Drinking Water Guidelines for chlorothalonil. Health and Welfare Canada have advised a guidance value of 30 ppb. This has not been given the thorough consideration that a guideline value would receive. The low frequency of detection may in part be due to the low water solubility of 1.2 mg/l at 25°C.

Metribuzin was detected in two of three samples analyzed. Metribuzin's water solubility is 1200 mg/l at 25°C and this may have contributed to the high frequency of detection. Further study with a greater number of samples would be required to confirm this detection frequency. All detectable concentrations were well below the Canadian Drinking Water Guidelines of 80 ppb.

Four of twenty one samples contained mancozeb. The detectable concentrations ranged from 32 ppb to trace levels. The high detection limit for mancozeb equivalent EDBC of 25 ppb and its rapid decay may have contributed to the comparatively low frequency of detection. The samples appeared to contain relatively high concentrations of mancozeb considering the per cent recovery. The lack of information on mancozeb, such as a guideline or guidance value, and an uncertainty in the accuracy of values reported for the spiked samples makes it difficult to comment meaningfully on the mancozeb results.

Nitrate samples indicated an average concentration of 4.8 mg/l, almost twice the provincial average of 2.5 mg/l. Wells with detectable residues of pesticide contained an average nitrate level of 5.9 mg/l. Of 43 samples, only two contained both bacteria and pesticide residue. A lack of accurate well information produced difficulties in correlating the bacteria, nitrate and pesticide data to well construction.

9.0 CONCLUSIONS AND RECOMMENDATIONS

1. Detectable residues of all four (4) pesticides investigated were found. Where guidance values are available, all results were within the recommended limits.

2. Due to the rapid decomposition of mancozeb the results are of questionable value. Analysis for metabolites may yield more accurate results.

3. The average concentration of nitrates in groundwater in the potato producing region of the province is higher than the average for the entire province. Although a limited number of samples were analyzed for this project, further study conducted under the Canada P.E.I. Water Management Agreement Nitrate Project supports this finding.

4. There is a need to develop analytic protocol, including lab reference standards for many pesticide compounds including all those in this report.

5. Further investigation of the occurrence of metribuzin is indicated from the frequency of occurrence in this survey.

6. Further investigation of the occurrence of other pesticide compounds is warranted. Due to their extensive use and high toxicity some suggested candidates are: MCPA, metalaxyl and fenvalerate, as well as metabolites of the pesticides studied in this report.

7. The reporting of the amount of individual pesticide products sold in the province each year by pesticide retailers and wholesalers would aid in the establishment of priority pesticides for further study.

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